This document contains Appendix D from the 2004 Holland America Veendam Data Report. Appendix D contains Data Review Narratives and Other Issues. The report and all the appendices for this sampling event can be downloaded from ***http://www.epa.gov/owow/oceans/cruise_ships/veendam.html***

Holland America Veendam

2004 Analytical Results

Appendix D

March 2006

Appendix D

DATA REVIEW NARRATIVES AND ISSUES ASSOCIATED WITH RESULTS FOR TOTAL CYANIDE VERSUS AVAILABLE CYANIDE

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6503

Data Validation Report For BOD_5 Samples

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

December 13, 2004

BOD_5 Method 405.1

Completeness

During Sampling Episode 6503 aboard the HAL Veendam, at total of 19 samples (excluding QC samples) were collected for analysis of 5-day Biochemical Oxygen Demand (BOD_5) by EPA Method 405.1. All 19 samples received by the laboratory were analyzed for BOD_5 for a completeness of 100% (all planned samples were collected and analyzed). Sample numbers for BOD_5 are provided in Table 1.

Table 1. BOD_5 Samples Collected During Sampling Episode 6503

Sample Numbers	Sample Point Description
65219, 65223, 65227,65231,65235	Treatment System Influent
65261, 65265, 65269, 65273, 65277, 65285, 65289	Treatment System Effluent
65207	Accommodations
65215	Galley
65202	Laundry
65211	Food Pulper
65291	Screening Solids
65292	Waste Biosludge
65295	Source Water

The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete BOD_5 data for the samples listed in Table 1.

Holding Times

Method 405.1 requires that all BOD_5 samples be analyzed within 48 hours following collection. Analysis of traffic reports and laboratory data sheets indicates 4 of the 19 BOD_5 samples were analyzed outside the 48 hour hold time window. Table 2 shows the sample numbers, the total hold time from collection to analysis, and the measured BOD_5 result for the four samples analyzed past the method-specified holding time.

Table 2. BOD_5 Samples Exceeding Hold Times

Sample Number	Sample Description	Sample Hold Time	Method Hold Time	BOD_5 Result
65235	Treatment System Influent	57.2 hours	48 hours	537 mg/L
65277	Treatment System Effluent	56.8 hours	48 hours	2.2 mg/L
65289	Treatment System Effluent	56.5 hours	48 hours	2.5 mg/L
65207	Accommodations	64.5 hours	48 hours	391 mg/L

To determine the impact of exceeding the holding times for these four samples, results of similar samples collected the same sampling point were reviewed. The BOD_5 concentration in the treatment system influent ranged from 481 mg/L to 786 mg/L. The BOD_5 concentration in the effluent samples ranged from <2 mg/L to 6 mg/L. Since the BOD_5 results for the samples that exceeded holding times are within the range of values reported for samples that did not exceed holding times, BOD_5 results from samples 65277, 65289, and 65235 should be considered valid for the cruise ship rulemaking.

The BOD_5 results from the accommodations wastewater sample can not be compared to similar data within the data set since only a single accommodations wastewater sample was collected. Accommodations wastewater is a component of the treatment system influent. Further, the holding time for this sample falls within the same period as the other samples that exceeded holding times. Consequently, the BOD_5 result from this sample should also be considered valid.

Calibration

The calibration of the BOD_5 test was performed with a method blank and glucose spiked blanks to verify seed effectiveness and analytical technique. Method blanks consist of potable water passed through an activated carbon bed to remove residual organic compounds. During Sampling Episode 6503, a total of 3 method blanks were prepared and analyzed for BOD_5. The results of the 3 method blank analysis showed BOD_5 concentrations less than 2 mg/L.

To verify seed effectiveness and analytical technique, method blanks were spiked with a sufficient amount of glucose to yield a theoretical BOD_5 concentration of 200 mg/L. Spiked method blanks are then analyzed for BOD_5 and results of the analysis, reported as percent recovery, are compared to the recovery limits for Method 405.1. Table 3 shows the results of the spiked samples. Results of the spike sample analyses indicate all recoveries are within the method-specified limits.

Table 3. Analysis of BOD_5 Recovery Data for Spiked Samples

Sample	Spike Result	Spike Level	Recovery	Recovery Limits
Method Blank	184 mg/L	200 mg/L	92%	60% - 140 %
Method Blank	154 mg/L	200 mg/L	77%	60% - 140%
Method Blank	166 mg/L	200 mg/L	83%	60% - 140%
Method Blank	167 mg/L	200 mg/L	84%	60% - 140%

Precision Analysis

Reproducibility for BOD_5 is measured as relative percent difference (RPD) between laboratory and field duplicate samples. Laboratory duplicate samples measure the precision of the method and analyst by comparing the results of two separate analyses of the same sample. Field duplicate samples measure the precision of the field sampling method by comparing the BOD_5 results for split samples prepared in the field. The QAPP for the Cruse Ship Rulemaking provides RPD targets for all laboratory duplicate samples and field duplicates samples as less than 20% and 30%, respectively.

Table 4 shows the RPD results for laboratory duplicate samples and a duplicate method blank spiked sample. The RPDs shown in Table 4 indicate the method blank spike sample is within the RPD and only one laboratory duplicate sample (65261) was outside the QAPP-specified target of less than 20%. Also, for sample 65273, the RPD cannot be calculated. For both samples, the BOD_5 concentration was near the detection limit of 2 mg/L, where analytical variability increases. Therefore, the associated variability between the sample result and its duplicate are acceptable for this program and the reported BOD_5 results are valid.

Table 4. Relative Percent Difference Between Laboratory Duplicate Samples

Sample No.	BOD_5 Result	Duplicate BOD_5 Result	RPD	RPD Target
Spiked Method Blank	184 mg/L	154 mg/L	17.8%	<20%
65231	481 mg/L	480 mg/L	0.2%	<20%
65273	2.05 mg/L	<2 mg/L	NA	<20%
65277	2.24 mg/L	2.39 mg/L	6.5%	<20%
65261	3.64 mg/L	2.63 mg/L	**32.2%**	<20%

NA: RPD can not be calculated since one or both of the sample results is less than the PQL.
RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
RPDs outside the QAPP target are represented in bold.

Table 5 shows the RPD results for field duplicate samples. RPDs for one sample pair in Table 5 is within the QAPP-specified target of less than 30%. For the second sample pair, RPD cannot be calculated because both results were reported as less than the detection limit. The field data precision is acceptable and the BOD_5 results are valid.

Table 5. Relative Percent Difference Between Field Duplicate Samples

Sample No.	BOD_5 Result	Sample No.	BOD_5 Result	RPD	RPD Target
65269	<2 mg/L	65285	<2 mg/L	NA	<30%
65277	2.24 mg/L	65289	2.49 mg/L	10.6%	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the PQL.
RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.

Data Quality Assessment

This data validation assessment indicates all the BOD_5 data collected during Sampling Episode 6503 can be used for the large cruise ship rulemaking effort.

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MEMORANDUM

DATE: January 10, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for Classical Analyses for the Alaska Cruise Ship Industry
Episode 6503

OVERVIEW

Under EPA Contract Number 68-C-03-068, Analytical Laboratory Services, Inc. (ALSI) submitted classical wet chemistry data for 25 samples in Episode 6503. Table 1 provides a complete listing of samples, matrices, and the analytes of interest.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analytes of Interest

EPA Sample #	Matrix	Sample Description	Sampling Date	Analytes
65202	Aqueous	SP1, Laundry wastewater	6/23/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65207	Aqueous	SP3, Accommodations wastewater	6/24/04	
65211	Aqueous	SP4, Food Pulper wastewater	6/22/04	
65215	Aqueous	SP5, Galley wastewater	6/22/04	
65219	Aqueous	SP6, Influent to wastewater treatment	6/21/04	
65223	Aqueous	SP6, Influent to wastewater treatment	6/22/04	
65227	Aqueous	SP6, Influent to wastewater treatment	6/23/04	
65228	Aqueous	SP6, Influent to wastewater treatment	6/23/04	HEM, SGT-HEM
65231	Aqueous	SP6, Influent to wastewater treatment	6/23/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65232	Aqueous	SP6, Influent to wastewater treatment	6/23/04	HEM, SGT-HEM

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analytes of Interest

EPA Sample #	Matrix	Sample Description	Sampling Date	Analytes
65235	Aqueous	SP6, Influent to wastewater treatment	6/25/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65261	Aqueous	SP9, Effluent from wastewater treatment	6/21/04	
65265	Aqueous	SP9, Effluent from wastewater treatment	6/22/04	
65269	Aqueous	SP9, Effluent from wastewater treatment	6/23/04	
65270	Aqueous	SP9, Effluent from wastewater treatment	6/23/04	HEM, SGT-HEM
65273	Aqueous	SP9, Effluent from wastewater treatment	6/23/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65274	Aqueous	SP9, Effluent from wastewater treatment	6/23/04	HEM, SGT-HEM
65277	Aqueous	SP9, Effluent from wastewater treatment	6/24/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65278	Aqueous	SP10, Effluent from wastewater treatment	6/24/04	HEM, SGT-HEM
65281	Aqueous	SP10, Effluent from wastewater treatment	6/21/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide
65283	Aqueous	SP10, Effluent from wastewater treatment	6/23/04	alkalinity, chloride, sulfate, TDS, TSS, total cyanide
65289	Aqueous	SP10, Effluent from wastewater treatment	6/25/04	ammonia-N, COD, nitrate/nitrite, total phosphorus, TKN, TOC
65291	Solid	SP11, Screening solid	6/22/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TOC, total cyanide, total solid, HEM, SGT-HEM
65292	Sludge	SP12, Waste biosludge (desludge)	6/22/04	
65295	Aqueous	SP15, Source water	6/21/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide

These data have been reviewed in accordance with SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004) and with the specifications listed in the contract. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary table (Table 2).

SUMMARY

All samples were successfully analyzed within the contract-specified holding times for all classical wet chemistry parameters specified in the sampling and analysis plan with the exception of sample 65207, which was analyzed outside of the contract-specified holding time for the COD analysis. The calibration and continuing calibration standards were successfully analyzed, where required by the methods. Laboratory blanks were performed for each analysis, and there was no contamination detected above the laboratory reporting limits. The QC samples, including the ongoing and precision recovery sample (OPR) and matrix spike/matrix spike duplicate (MS/MSD) samples, demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below.

DATA ISSUES: CHEMICAL OXYGEN DEMAND (COD)

Holding Times

Sample 65207 was initially analyzed within the holding time for COD; however, this sample result exceeded calibration range and required dilution. The dilution analysis was performed 3 days after the holding time had expired. Therefore, SCC considers the COD result of 541 mg/L in sample 65207 to be an estimated value.

DATA ISSUES: AVAILABLE CYANIDE GREATER THAN TOTAL CYANIDE

Sample Results

For all samples in this episode, SCC evaluated total cyanide results against available cyanide results, and found that available cyanide was detected in samples 65207, 65219, 65227, 65231, 65235, 65265, 65281, and 65295, while total cyanide were not detected in these samples. In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. However, for these samples, it is important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the available cyanide determination was performed by a different laboratory. In addition, the overall homogeneity of the waste stream being sampled can have a significant effect on the cyanide results. Therefore, it may not be possible to identify problems that would invalidate one cyanide fraction or the other.

A review of the traffic reports (TRs) for the samples indicates that some of the samples in Episode 6503 were not treated with lead carbonate to remove sulfides. SCC consulted EPA and the sampling contractor and determined that the following 11 samples were not treated with lead carbonate:

65202, 65207, 65211, 65227, 65231, 65235, 65269, 65273, 65277, 65283, and 65295

Three sets of matrix spike/matrix spike duplicate (MS/MSD) samples were prepared for total cyanide analysis on samples 65207 (accommodations wastewater), 65269 (an effluent), and 65273 (an effluent). The MS/MSD recoveries for the three aqueous MS/MSD pairs were below the acceptance limits:

- 22% and 21% for sample 65207,
- 30% and 33% for sample 65269, and
- 5% and 1% for sample 65273

suggesting a potential for low bias in the total cyanide results for the associated aqueous samples.

The recoveries for the laboratory control samples (LCS, OPR, or QC check sample) analyzed along with the field samples were acceptable, indicating that the laboratory's overall analytical process was in control and suggesting either problems with the distillation process or an interference present in the sample matrix. Because the focus of the EAD analytical contracts is on effluent samples and because there are no acceptance criteria for aqueous matrices other than effluents, no MS/MSD analyses were performed on samples representing influents to the treatment process.

The total cyanide result for Sample 65273 (effluent) was reported as a non-detect at 5 µg/L and available cyanide was a non-detect at 2 µg/L. An MS/MSD pair for available cyanide was prepared from this sample and had recoveries of 101% and 102% respectively, while the MS/MSD recoveries for total cyanide were 5% and 1%, as noted earlier. This suggests a significant potential for low bias in the total cyanide result. Therefore, based on the low MS/MSD recoveries for total cyanide in this sample, the total cyanide non-detect is considered a minimum value and the available cyanide result is considered acceptable without qualification.

There were nine other samples in Episode 6503 that exhibited the pattern of total cyanide results less than the available cyanide results. Samples 65219, 65227, 65231, and 65235 are influents to treatment and, as noted above, there are no MS/MSD analyses that demonstrate the performance of either method for this matrix type. Samples 65227, 65231, and 65235 also are among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and given the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for samples 65227, 65231, and 65235 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples. Sample 65219 was treated in the field, therefore SCC recommends including both cyanide results for sample 65219 in the database, but flagging them to indicate the irreconcilable differences.

The total cyanide results for Sample 65207 (accommodations wastewater) were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 15.7 µg/L. The MS/MSD recoveries for total cyanide were 21% and 22%, as noted earlier. Sample 65207 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, given the low MS/MSD recoveries for total cyanide in this sample and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65207 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65211 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Total cyanide was detected at 14 µg/L, while available cyanide was reported at 88.4 µg/L. Sample 65211 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging

both cyanide results for sample 65211 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65295 is listed as a source water sample, a matrix type that should not present significant analytical difficulties. Sulfide was not detected in this sample by the field test performed at the time of collection and therefore, this sample is among the 11 samples that were not treated with lead carbonate. Although the presence of available cyanide at 19 µg/L in the source water is unexpected, there is no analytical evidence to suggest that the available cyanide result be excluded. However, an engineering review or other information not available to SCC may lead to a different conclusion. Therefore, SCC recommends including both cyanide results for sample 65295 in the database, but flagging them to indicate the irreconcilable differences.

Episode 6503 included two sets of field duplicate samples that were sent to the laboratories blind. SCC does not normally evaluate the agreement between field duplicate samples. However, because of concerns about the cyanide data, at EPA's request, SCC obtained information about the field duplicates from the sampling contractor and performed some simple comparisons. The two field duplicate pairs were samples 65261 and 65281, and samples 65265 and 65283, all effluent samples. The total cyanide results in sample 65261 were reported as a non-detect at 5 µg/L, while available cyanide was reported as a non-detect at 2 µg/L. For sample 65281, the blind field duplicate, the total cyanide results were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 8.96 µg/L. A similar pattern occurs for the cyanide results in the other field duplicate pair. Total cyanide was reported as a non-detect at 5 µg/L in both samples 65265 and 65283, while available cyanide was detected at 5.86 µg/L in sample 65265 and as a non-detect a 2 µg/L in sample 65283.

The MS/MSD recoveries for total cyanide in effluent sample 65273 were very low (1% and 5%), and low (33% and 30%) in sample 65269, suggesting a potential negative basis that may affect the total cyanide results in samples 65261, 65281, 65265, and 65283. Therefore, SCC recommends that the total cyanide results in sample 65261 and 65281 be considered minimum values. The difference between the available cyanide results in the two field duplicate samples (e.g., a non-detect at 2 µg/L and a detect at 8.96 µg/L) cannot be explained on the basis of the MS/MSD results for available cyanide in sample 65273, which was also an effluent. Given the discrepancy between the field duplicate results for available cyanide, SCC recommends including the available cyanide results for samples 65261 and 65281 in the database, but flagging them to indicate the irreconcilable differences. SCC recommends that the total cyanide results for samples 65261 and 65281 also be flagged to indicate the irreconcilable differences, as a further precaution.

Because of the low MS/MSD recoveries in the other effluent samples, the total cyanide result for sample 65265 is considered a minimum value. The available cyanide result of 5.86 µg/L is well within 30% of the reported detection limit for total cyanide (e.g., 5 µg/L), and therefore would normally not be qualified. However, because the available cyanide result in the field duplicate of the sample, 65283 is a non-detect at 2 µg/L, SCC recommends including both the total and available cyanide results for sample 65265 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65283 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Given the very low MS/MSD recoveries for total cyanide in effluent samples in this episode, SCC recommends flagging both cyanide results for sample 65283 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples.

The samples were analyzed for available cyanide by Bayer Laboratory. A separate data narrative has been prepared for the available cyanide analysis.

TECHNICAL NOTES:

Total Cyanide

For total cyanide, the solid samples 65291 and 65292 were prepared and analyzed as aqueous samples, due to the low percent solids content. Therefore, the data were included in the database as aqueous samples, as reported by the laboratory.

Silica Gel Treated N-Hexane Extractable Material (SGT-HEM)

Samples 65261, 65265, 65269, 65270, 65273, and 65274 were not analyzed for SGT-HEM because the HEM results were non-detects. At EPA's request, SCC created SGT-HEM records in the database, but the results for SGT-HEM are reported as NA, with the SCC qualifier reading "SGT-HEM was not analyzed because HEM was a non-detect."

If you have any questions regarding the analyses of these samples or the review of these data, please contact me by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6503 **Analysis:** Classicals

Industry: Alaska Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65207	COD	Estimated value	Holding time exceeded	NA	541 mg/L
65207	Total cyanide	—	Sample not treated with lead carbonate to remove sulfides. Low MS/MSD recoveries for total cyanide. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.	MISCA	ND
65211	Total cyanide	—	Samples not treated with lead carbonate to remove sulfides. No matrix-specific performance data. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.	MISCA	0.014 mg/L
65219	Total cyanide	—	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.	IRR	ND
65227	Total cyanide	—	Samples not treated with lead carbonate to remove sulfides. No matrix-specific performance data. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.	MISCA	ND
65231	Total cyanide				
65235	Total cyanide				
65261	Total cyanide	—	Total cyanide qualified as minimum value. Based on field duplicate results, irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.	IRR	ND
65265	Total cyanide	—			
65273	Total cyanide	Minimum value	Low MS/MSD % recoveries	NA	ND
65281	Total cyanide	Minimum value	Total cyanide qualified as minimum value. Based on field duplicate results, irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.	IRR	ND
65283	Total cyanide	—	Total cyanide qualified as minimum value. Sample not treated with lead carbonate to remove sulfides. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.	MISCA	ND
65295	Total cyanide	—	Irreconcilable results for total and available cyanide.	IRR	ND

ND = Non-detect at the laboratory's reporting limit. See the level in the database.
NA = Not applicable
MIN = Minimum value
IRR = Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
MISCA = Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.

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MEMORANDUM

DATE: March 31, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Jody Donnelly, Quality Assurance Chemist JHD
Sample Control Center

SUBJECT: Data Review Narrative for Dioxin/Furan Analysis for the Alaskan Cruise Ship Industry, Episode 6503

OVERVIEW

Under CSC Purchase Order 637415SSD, Axys Analytical Services submitted data for the analysis of dioxins and furans by EPA Method 1613B for two solid samples in Episode 6503. Table 1 provides a list of the samples, matrix, sample descriptions, and the required analytical method.

Table 1 - Sample Identifier, Description, Sampling Date, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6503	65293	Solid	SP1, Incinerator ash	06/20/04	1613B
6503	65294	Solid	SP1, Incinerator ash	06/20/04	1613B

These data have been reviewed in accordance with SCC's Data Review Guidelines for Dioxin/Furan Analysis by Method 1613B (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

Samples were successfully extracted and analyzed for the target analytes in EPA Method 1613B within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for the analysis detected no contamination above the laboratory's reporting limits. The QC samples, including the ongoing precision and recovery (OPR) samples, demonstrated that laboratory performance for these analyses was acceptable.

Reporting Limits

The samples were extracted using approximately 5 grams instead of the method-specified 10 grams. As a result, the minimum levels (MLs) provided in the database for samples 65293 and 65294 increased by approximately a factor of 2. The laboratory's past experience with ash samples shows that they tend to have significant matrix interference, which is why the sample size was reduced. Because the laboratory calibrated their instrument to 5 times lower than the lowest calibration standard specified in Method 1613B, the difference in sample size has no impact on the quality of the data. The MLs provided in the database for these samples reflect the smaller sample size.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Some analytes in samples 65293 and 65294 were qualified by SCC with a "J" flag, which indicates an estimated result that is below the laboratory's reporting limit but above the method detection limit. These analytes are annotated as such in the database and are detailed in Table 2.

Sample Reanalysis - Labeled Compound Recoveries

Sample 65294 was reextracted and reanalyzed (e.g., a new aliquot of the original sample was extracted) due to low labeled compound recoveries in the initial analysis. The reextraction was performed within method-specified holding times and the results met the acceptance limits for the labeled compounds. Therefore, the results for sample 65294 in the database as those from the reanalysis.

If you have any questions regarding the analysis of these samples or the review of these data, please contact me, by telephone at (703) 461-2203 or by facsimile at (703) 461-8056.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6503 **Analysis:** Method 1613B

Industry: Alaskan Cruise Ship **Reviewer:** J. Donnelly

Sample	Analyte	Action	Reason	SCC Qual	Level (ng/kg)
65293	2,3,7,8-TCDD	Estimated value	Analyte detected below laboratory's reporting limit but above method detection limit	J	1.63
	1,2,3,6,7,8-HxCDD				6.12
	1,2,3,7,8,9-HxCDD				9.34
65294	2,3,7,8-TCDD	Estimated value	Analyte detected below laboratory's reporting limit but above method detection limit	J	1.37
	1,2,3,7,8-PeCDD				6.40

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MEMORANDUM

DATE: December 16, 2004

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for Dioxin/Furan Analyses for the Alaskan Cruise Ship Industry
Episode 6503

OVERVIEW

Under EPA Purchase Order EP-C-04-047, Axys Analytical Services submitted data for the analysis of dioxins/furans by EPA Method 1613B for two aqueous samples in Episode 6503. Table 1 provides a complete listing of samples, matrices, sample descriptions, and the required analytical method.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Methods

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6503	65202	Aqueous	SP1, Laundry Wastewater	6/23/04	1613B
	65206	Aqueous	SP1, Laundry Wastewater	6/23/04	1613B

These data have been reviewed in accordance with SCC's Data Review Guidelines for Dioxins/Furans Analyses (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

All samples were successfully extracted and analyzed for the target analytes in EPA Method 1613B within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for the analysis detected no contamination above the laboratory's reporting limits. Instead of using the method-specified clean up procedure, all samples were processed by an automated clean up procedure that employs the Fluid Management System Inc., *"Power-Prep™ System,"* using standard chromatographic clean up columns. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable. None of the dioxins/furans were detected in either sample in this episode.

Reporting Limits

The laboratory's reporting limits are at the method-specified minimum levels (MLs). All samples were extracted using less than the method-specified 1000-mL aliquot, due to volume constraints. This variation in sample size increased the MLs for these samples by as much as 10%. As reported by the laboratory, the MLs provided in the database for these samples reflect the smaller sample volumes.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

If you have any questions regarding the analyses of these samples or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6503

Data Validation Report For Microbiological Analyses

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

January 27, 2005

Enterococci by MPN Method ASTM D6503-99
Fecal Coliform by MF SM 9222D
***E. Coli* by MPN Enzyme Substrate SM 9223B**

Completeness

During Sampling Episode 6503, a total of 66 samples (excluding QC samples) were collected for analysis of enterococci, fecal coliform, and *E. coli* by the methods listed above. Sample numbers ranged between 65202 and 65311. The number of grab samples collected for microbiologicals analyses was reduced from that described in the SAP because of capacity limitations of the onboard laboratory. ERG collected and analyzed as many microbiologicals samples as feasible, with an emphasis on wastewater treatment samples. EPA considers the microbiologicals dataset to be representative of the wastestreams sampled and acceptable for use in technical analyses.

The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete microbiological data for all submitted samples. Only one sample (Sample No. 65246) was not analyzed for all three types of bacteria, resulting in an analytical completeness of greater than 99%. A list of the samples collected and analyzed during Sampling Episode 6503 is provided in Table 1.

Table 1. List of Samples and Required Microbiological Analyses for Sampling Episode 6503

Sample Numbers	Sample Point Description
65219, 65220, 65221, 65222, 65223, 65224, 65225, 65227, 65228, 65231, 65232, 65234, 65235, 65236, 65237, 65310	Influent to Treatment
65241, 65242, 65243, 65244, 65245, 65246*, 65247, 65249, 65250, 65253, 65254, 65256, 65257, 65258, 65259, 65304	Influent to UV Disinfection
65261, 65262, 65263, 65264, 65265, 65266, 65267, 65269, 65270, 65273, 65274, 65276, 65277, 65278, 65279, 65281, 65283, 65287, 65288, 65289, 65302, 65303, 65305, 65311	Effluent from Treatment
65205	Laundry
65207	Accommodations
65211, 65212	Food Pulper
65215	Galley
65295, 65296, 65297, 65298, 65299	Source Water

* Analyzed for only *E. Coli* and fecal coliform.

Holding Times

The QAPP developed for the cruise ship rulemaking requires all microbiological samples be analyzed within 6 hours following collection. Analysis of traffic reports and laboratory data sheets indicates all microbiological samples submitted field laboratory for analysis were analyzed within 6 hours following collection.

Detection Limits

Some microbiological results were reported by Analytica Alaska as "greater than" a specified value (e.g., >600,000,000 CFU/100 mL). These results are qualified in the analytical database by a ">" flag and are listed in Table 2. This qualifier indicates the sample was not diluted sufficiently (i.e., the measured concentration exceeds the range of dilutions). The reported results in the database are the upper limit of the measurement range, and the ">" flag indicates that the actual concentrations are some level greater than the reported upper limit. Although the results are valid, data users should consider this data qualification in using the data.

Table 2. Microbiological Sample Results with ">" Qualifier

Analysis	Sample Numbers
Enterococci	65219, 65221, 65224,
E. Coli	65219, 65220, 65221, 65224, 65225

During onboard analysis, one effluent from treatment sample for enterococci analysis (sample 65262) was overly diluted to a level which generated a non-detect (ND) result, but with a detection limit (1,000 MPN/100 mL) much greater than both the expected concentration in the sample and the typical detection limit of 1 MPN/100 mL. Although the result is valid, its use for engineering analyses is limited due to the high detection limit.

Calculation of Fecal Coliform Density

Fecal coliform density should be computed from sample quantities that produced membrane filtration counts within the desired range of 20 to 60 fecal coliform colonies. This was not always possible for many cruise vessel samples for various reasons. First, many samples, such as wastewater treatment effluent samples, had low concentrations of microbiological contaminants, and the occurrence of fecal coliform colonies was minimal. In these cases, as specified by the method, the analyst counted all fecal coliform colonies, disregarding the lower limit of 20.

Second, most samples (other than wastewater treatment effluent) required a series of sample dilutions to obtain between 20 and 60 colony forming units per filter pad. In most cases, the analyst obtained a result within this range using one of the prepared dilutions. However, in a few instances, no single filter generated a result within the desired range (i.e., two results within

the desired range, two results either above or below the desired range, one result above and one result below the desired range, etc). In these cases, as specified by the method, the analyst totaled the counts on the two filters and reported the result as a number per 100 mL. Table 3 lists the fecal coliform samples for Sampling Episode 6503 that did not yield a single result within the desired range, and for which the analyst computed the number of colony forming units based on a calculation of the results from multiple plates. Calculations for these samples are provided in the Cruise Ship Rulemaking Record.

Table 3. Fecal Coliform Samples For Which Multiple Plates Were Used to Compute CFU/mL

Sample Number	Sample Description
65207	Accommodations Wastewater
65234	Influent to UV Disinfection
65237	Influent to Treatment
65253, 65259, 65304	Influent to UV Disinfection

In summary, calculation of fecal coliform density was performed as specified by the method, and the reported results are valid.

Laboratory QC Measures

QC measures for microbiologicals include positive and negative controls, media sterility checks, dilution water sterility checks, sample bottle blanks, membrane filter preparation blanks, and verification of incubator temperatures. The following describes the results of each of these QC checks used during Sampling Episode 6503. (The actual QC results are contained in Analytica Alaska's laboratory report, which is provided in the Cruise Ship Rulemaking Record.)

Positive and Negative Controls

Positive and negative controls are known cultures that are analyzed exactly like the field samples, and will produce an expected positive or negative result for a given type of medium. For Sampling Episode 6503, one medium-specific positive and negative control was analyzed for each medium lot used. Results of the positive and negative controls indicate the media used by the field laboratory for Sampling Episode 6503 produced expected results.

Media Sterility Checks

Media are checked for sterility by incubating the media at the appropriate temperature without sample and observed for growth. For Sampling Episode 6503, one medium sterility check was performed for each medium lot used. The media sterility check verified the media used by the field laboratory had not been contaminated with any of the microorganisms being analyzed for this work.

Dilution Water Sterility Checks

Dilution water is analyzed exactly like a field sample and observed for growth of fecal coliform, *E. coli*, and enterococci to verify the water is not contaminated with these organisms prior to use. For Sampling Episode 6503, one sample dilution blank was analyzed for each lot of dilution water used. Results of dilution water blank analysis verified the water had not been contaminated with any of the microorganisms being analyzed for this work.

Sample Bottle Blank

A sample bottle blank was analyzed for each bottle lot used during Sampling Episode 6503 to determine adequate bottle sterilization prior to use by the sampling crew. Results of the sample bottle blank (dilution water poured into the sample bottle and analyzed) verified the sample bottles had not been contaminated with any of the microorganisms being analyzed for this work.

Membrane Filter Preparation Blank

Membrane filter blanks were analyzed at the beginning of each set of filtered samples to document adequate sterilization of membrane filtration equipment. Membrane blanks verified that the equipment used for filtration during Sampling Episode 6503 had not been contaminated with any of the microorganisms being analyzed for this work.

Incubator Temperature

Incubator temperatures were monitored in the onboard laboratory to verify that prepared microbiological samples were being incubated at the correct temperatures. Review of the laboratories incubator log sheets generated during Sampling Episode 6503 verified the temperature was measured and recorded twice daily, no less than four hours apart, and the temperature checks were ±0.5°C apart.

Precision Analysis

Reproducibility for the microbiological analyses is measured as relative percent difference (RPD) between duplicate samples. The QAPP for the Cruse Ship Rulemaking presents the target RPD for all laboratory and field duplicate samples as less than 20% and 30%,

respectively. During Sampling Episode 6503, additional 100-ml sample volumes were collected for a number of grab samples with the intent that the laboratory would prepare a single composite and then analyze duplicate samples from the composite to evaluate laboratory precision (i.e., laboratory duplicates). The laboratory did not prepare a composite, but instead analyzed each of the 100-ml sample volumes individually. Because a composite was not prepared, laboratory precision could not be evaluated. The results obtained from analysis of these individual sample volumes are field duplicates, not laboratory duplicates, and because they were collected as laboratory duplicates, the original sample and the duplicate sample have the same sample number. In order to differentiate the original from the duplicate, ERG assigned new SCC numbers (65302, 65303, 65304, 65305, 65310, and 65311) to the duplicate samples.

During Sampling Episode 6503, five additional sets of intended field duplicate samples (i.e., different sample numbers) were also collected and analyzed by each of the three microbiological methods. These field duplicate samples were prepared to determine the precision of the field sampling equipment. Duplicate sample data for the samples described above, along with the five intended field duplicate samples, are provided for *E. coli*, fecal coliform, and enterococci in Tables 4, 5 and 6.

Table 4. *E. Coli* Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65261	65281	ND	ND	NA	<30%
65265	65283	ND	ND	NA	<30%
65273	65287	ND	ND	NA	<30%
65274	65288	ND	ND	NA	<30%
65277	65289	ND	ND	NA	<30%
65264	65302*	ND	ND	NA	<30%
65267	65303*	ND	ND	NA	<30%
65259	65304*	75.4 MPN/100mL	77.1 MPN/100mL	2.2%	<30%
65279	65305*	ND	ND	NA	<30%
65224	65310*	>2,420,000 MPN/100mL	75,900 MPN/100mL	NA	<30%
65276	65311*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less and/or greater than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 1 MPN/100 mL.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

Table 5. Fecal Coliform Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65261	65281	ND	ND	NA	<30%
65265	65283	ND	ND	NA	<30%
65273	65287	ND	ND	NA	<30%
65274	65288	ND	ND	NA	<30%
65277	65289	ND	ND	NA	<30%
65264	65302*	ND	ND	NA	<30%
65267	65303*	ND	ND	NA	<30%
65259	65304*	18.2 CFU/100mL	8.2 CFU/100mL	**76%**	<30%
65279	65305*	ND	ND	NA	<30%
65224	65310*	14,500,000 CFU/100mL	3,600,000 CFU/100mL	**120%**	<30%
65276	65311*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 1 CFU/100ml.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

Table 6. Enterococci Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65261	65281	ND	ND	NA	<30%
65265	65283	ND	ND	NA	<30%
65273	65287	ND	ND	NA	<30%
65274	65288	5.10 MPN/100mL	ND	NA	<30%
65277	65289	ND	ND	NA	<30%
65264	65302*	ND	ND	NA	<30%
65267	65303*	ND	ND	NA	<30%
65259	65304*	60.8 MPN/100mL	35.4 MPN/100mL	**52.8%**	<30%
65279	65305*	ND	ND	NA	<30%
65224	65310*	>2,420,000 MPN/100mL	201,000 MPN/100mL	NA	<30%

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65276	65311*	1 MPN/100mL	1 MPN/100mL	0%	<30%

NA: RPD can not be calculated since one or both of the sample results is less and/or greater than the laboratory reporting limit.

ND: Measured concentration less than the laboratory reporting limit of 1 MPN/100 mL.

Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.

*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

The data provided in Tables 4, 5, and 6 show that approximately 90% of the field duplicate samples analyzed by the laboratory gave nearly the same measured values. Two duplicate fecal coliform analyses and one duplicate enterococci analysis had RPDs outside the QAPP-specified target of less than 30%. All of these results were from a sample collected at the influent to the disinfection system. Data users should consider limitations in the precision of these microbiological analyses of untreated wastewater as they use the results.

One duplicate sample analyzed for enterococci (Sample Number 65274) measured 5.1 MPN/100 mL in the first sample and <1 MPN/100 mL in the second sample. The RPDs for this sample pair, as well as for a number of other samples could not be calculated because one or both of the duplicate sample results was less than the laboratory reporting limit. Although the RPD for these samples cannot be calculated, the microbiological analysis precision is acceptable for this program and the reported microbiological results are valid.

Data Quality Assessment

This data validation assessment indicates all the microbiological data collected during Sampling Episode 6503 can be used for the large cruise ship rulemaking effort.

Data users should consider limitations in the precision of microbiological analyses of untreated wastewater, as well as sample results derived from overly high or low sample dilution, as they use the data.

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MEMORANDUM

DATE: December 16, 2004

TO: Don Anderson, Project Officer
EPA EAD

FROM: Julie Rest, Quality Assurance Chemist
Sample Control Center

SUBJECT: Data Review Narrative for Total and Dissolved Metals Analyses for the Alaskan Cruise Ship Industry, Episode 6503

OVERVIEW

Under EPA contract number 68-C-03-045, Southwest Research Institute (SWRI) submitted data for the analysis of total and dissolved metals by EPA Methods 200.7, 200.8, 245.1, and 245.5 in Episode 6503. The 18 aqueous samples and 3 solid samples in this episode were analyzed for 24 metals by Method 200.7 (ICP-AES) and for selenium and thallium by Method 200.8 (ICP-MS). Mercury analyses of the aqueous samples were performed by Method 245.1, and by Method 24.55 for the solid samples. Table 1 provides a list of samples, matrices, sampling dates, and the required analytical methods.

All of the aqueous samples were analyzed for both total and dissolved forms of the metals. The three solid samples were analyzed for total metals. The laboratory added the suffixes "D" and "T" to the sample numbers on the hard copy reports to differentiate the analyses for dissolved metals and total metals, respectively. These suffixes are also used in this data review narrative. However, the sample numbers in the database will not contain these suffixes. Consistent with current EAD protocols, the total and dissolved metals distinctions are provided in the "procedure" field of the database.

This episode included data for two matrix spike/matrix spike duplicate (MS/MSD) pairs for aqueous effluent samples, and one MS/MSD pair for the solid samples.

Table 1 - Sample Identifiers, Descriptions, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65202	Aqueous	SP1, Laundry waste	6/23/04	200.7, 200.8, and 245.1
65207	Aqueous	SP3, Accommodations wastewater	6/24/04	
65211	Aqueous	SP4, Food pulper	6/22/04	
65215	Aqueous	SP5, Galley wastewater	6/22/04	
65219	Aqueous	SP6, Influent to wastewater treatment	6/21/04	
65223	Aqueous	SP6, Influent to wastewater treatment	6/21/04	
65227	Aqueous	SP6, Influent to wastewater treatment	6/23/04	
65231	Aqueous	SP6, Influent to wastewater treatment	6/24/04	
65235	Aqueous	SP6, Influent to wastewater treatment	6/25/04	
65261	Aqueous	SP9, Effluent from wastewater treatment	6/21/04	
65265	Aqueous	SP9, Effluent from wastewater treatment	6/22/04	

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Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Table 1 - Sample Identifiers, Descriptions, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65269	Aqueous	SP9, Effluent from wastewater treatment	6/23/04	200.7, 200.8, and 245.1
65273	Aqueous	SP9, Effluent from wastewater treatment	6/24/04	
65277	Aqueous	SP9, Effluent from wastewater treatment	6/25/04	
65281	Aqueous	SP10, Effluent from wastewater treatment	6/21/04	
65285	Aqueous	SP10, Effluent from wastewater treatment	6/23/04	
65291	Solid	SP11, Screening Solids	6/22/04	200.7, 200.8, and 245.5
65292	Solid	SP12, Waste Biosludge	6/22/04	
65293	Solid	SP13, Incinerator Ash	6/21/04	
65295	Aqueous	SP15, Source water	6/21/04	200.7, 200.8, and 245.1
65301	Aqueous	SP17, Equipment blank	6/20/04	

These data have been reviewed in accordance with SCC's Data Review Guidelines for Metals Analyses (November 2004) and with the specifications listed in EPA Methods 200.7 (Rev. 5), 200.8 (Rev. 5.4), 245.1 (03/83), and 245.5 (03/83). All data are of acceptable quality with the qualifiers described below and detailed in the data review summary table (Table 2).

Following SCC's initial review of the data, EPA inquired about modifying the reporting convention used for metals to address EPA's need to compare sample results to the water quality criteria for Alaskan coastal waters. The current EAD metals contracts specify that the laboratory report results down to the minimum level (ML) for each analyte. By examining both the hard copy raw data and the laboratory's electronic submission, SCC determined that results between the ML and the method detection limit (MDL) were available for all of the metals. After consultation with EPA, SCC modified the reported results such that any analytes not detected in the sample were reported as a non-detect at the laboratory's MDL rather than at the ML. As a result, there are also some analytes that are reported as detected between the ML and the laboratory's MDL. These results are flagged "J" in the database. This change also means that the hard copy data reported by the laboratory may not match the results in the database for values in the database between the MDL and ML of the analyte. This change also necessitated an additional review of all of the blank results to ensure that the low-level results reported in samples were not simply artifacts of the blanks.

SUMMARY

All 21 samples were successfully analyzed within the specified holding times. The initial precision and recovery analyses and the MDL study were performed and met the specified criteria. Calibration curves, calibration standards, and calibration blanks and preparation blanks were successfully analyzed. Some elements were detected in blanks above the MDLs, but none were found above the laboratory's reporting limits or minimum levels. For Method 200.8, instrument tuning reports and internal standard data indicate that the system was in control. QC samples, including the laboratory control sample, matrix spike sample, matrix duplicate sample, and laboratory serial dilution sample demonstrated that laboratory performance for these analyses was acceptable, with the exception of the issue described below.

DATA ISSUES

Blanks

One or more elements were detected in the preparation blanks and some of the continuing calibration blanks (CCBs) associated with the samples in this episode at concentrations greater than the respective MDLs but less than the method-specified MLs. (Note: This is a function of the change in reporting limits requested by EPA after the fact and not an issue of laboratory performance.) The data quality is affected as follows:

- Sample Results Less than Five Times Blank Results: When the sample result is less than five times the blank result, there are no means by which to ascertain whether or not the presence of the analyte may be attributed to contamination. Therefore, SCC recommends that the data be reported in the database as a non-detect at the MDLs, adjusted sample size, dilution, and matrices. These instances are detailed in the attached data review summary table.

- Sample Results Greater than Five Times but Less than Ten Times Blank Results: SCC considers these results to be of acceptable quality, but they may be maximum values. These instances are detailed in the attached data review summary table.

- Sample Results Greater than Ten Times Blank Results or Analyte Not Detected in Sample: SCC does not consider the presence of the analyte in the blank to adversely affect the data in cases where the sample results are greater than ten times the associated blank results or where the analyte is not detected in associated samples. Because SCC considers such data to be acceptable without qualification, these cases do not merit further detail.

Matrix Spike/Matrix Spike Duplicate

Silver was recovered above the method-specified criteria and antimony was recovered below the method-specified criteria in the MS/MSD prepared for sample 65293. The relative percent difference exceeded the criteria in the MS/MSD for both analytes. Both of these analytes were detected in this sample, and therefore, SCC believes that the results for antimony and silver in sample 65293 should be considered estimated values.

TECHNICAL NOTES

According to the laboratory narrative, due to low percent solids in samples 65291 and 65292, these two samples were prepared and analyzed as aqueous samples for the Method 200.7 and 200.8 analyses, but as solid samples for the Method 245.5 analysis.

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's Data Review Team Leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachment

cc: Marla Smith, EPA
Beverly Randolf, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodie King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6503 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
Total 65202, 65211, 65215, 65231, 65261, 65265, 65269, 65281, 65301	Hg	Report in database as non-detects	Sample results <5x blank results	NA	ND
Total 65207, 65219, 65223, 65227, 65273, 65277, 65285, 65295	Hg	Maximum values	Sample results >5x but <10x blank results	NA	See database report
Dissolved 65301	Hg	Report in database as non-detects	Sample results <5x blank results	NA	ND
Dissolved 65202, 65211, 65215, 65261, 65265, 65269, 65281	Hg	Maximum values	Sample results >5x but <10x blank results	NA	See database report
Total 65202, 65261, 65265, 65269, 65273, 65277, 65281, 65285	B	Report in database as non-detects	Sample results <5x blank results	NA	ND
Total 65215, 65219, 65223, 65295	B	Maximum values	Sample results >5x but <10x blank results	NA	See database report
Dissolved 65281, 65207	V	Report in database as non-detects	Sample result <5x blank results	NA	ND
Total 65202	Ba	Maximum value	Sample result >5x but <10x blank result	NA	See database report
Total 65202, 65219, 65223, 65227, 65231, 65235	V	Report in database as non-detects	Sample result <5x blank results	NA	ND
Total 65291, 65292	Mo	Maximum values	Sample results >5x but <10x blank results	NA	See database report
Total 65207	V	Maximum values	Sample results >5x but <10x blank results	NA	See database report
Total 65211, 65291, 65292	Be	Report in database as non-detects	Sample result <5x blank results	NA	ND

Table 2
Data Review Summary Table

Episode: 6503 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
Total 65211, 65231, 65235	Mo	Report in database as non-detects	Sample result <5x blank results	NA	ND
Dissolved 65211	Mo	Report in database as non-detects	Sample result <5x blank results	NA	ND
Dissolved 65202, 65261, 65265, 65269, 65273, 65281, 65285, 65301	B	Report in database as non-detects	Sample result <5x blank results	NA	ND
Dissolved 65207, 65215, 65235, 65295	B	Maximum values	Sample results >5x but <10x blank results	NA	See database report
Total 65291, 65292	Y	Report in database as non-detect	Sample result <5x blank results	NA	ND
Dissolved 65231	Sn	Report in database as non-detect	Sample result <5x blank results	NA	ND
Total 65293	Ag	Estimated value	MS/MSD % recoveries above criteria; RPD exceeded criteria	NA	15.4 mg/kg
Total 65293	Sb	Estimated value	MS/MSD % recoveries below criteria; RPD exceeded criteria	NA	28.3 mg/kg

NA = Not applicable
ND = Not detected

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MEMORANDUM

DATE: December 16, 2004

TO: Don Anderson, Project Officer
EPA EAD

FROM: Julie Rest, Quality Assurance Chemist
Sample Control Center

SUBJECT: Data Review Narrative for Organics Analyses for the Alaskan Cruise Ship Industry, Episode 6503

OVERVIEW

Under EPA Contract Number 68-C-03-033, Pacific Analytical, Inc. (PAI) submitted data for the analysis of volatiles by Method 624 and semivolatile organics by Method 625 in Episode 6503. Table 1 provides a list of samples, sampling dates, matrices and the required analytical methods. This episode included two solid samples and eighteen aqueous samples for Method 624 analysis, and three solid samples and eighteen aqueous samples for Method 625 analysis. The package included data for three matrix spike (MS) and matrix spike duplicate (MSD) pairs for Method 625 analysis and one MS/MSD pair for Method 624 analysis.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65202	Aqueous	SP1, Laundry	6/23/04	624, 625
65207	Aqueous	SP3, Accommodations, Graywater	6/24/04	624, 625
65211	Solid	SP4, Food Pulper	6/22/04	624, 625
65215	Aqueous	SP5, Galley wastewater	6/22/04	624, 625
65219	Aqueous	SP6, Influent to wastewater treatment	6/21/04	624, 625
65223	Aqueous	SP6, Influent to wastewater treatment	6/22/04	624, 625
65227	Aqueous	SP6, Influent to wastewater treatment	6/23/04	624, 625
65231	Aqueous	SP6, Influent to wastewater treatment	6/24/04	624, 625
65235	Aqueous	SP6, Influent to wastewater treatment	6/25/04	624, 625
65261	Aqueous	SP9, Effluent from wastewater treatment	6/21/04	624, 624
65265	Aqueous	SP9, Effluent from wastewater treatment	6/21/04, 6/22/04	624, 625
65269	Aqueous	SP9, Effluent from wastewater treatment	6/23/04	624, 625
65273	Aqueous	SP9, Effluent from wastewater treatment	6/28/04, 6/24/04	624, 625
65277	Aqueous	SP9, Effluent from wastewater treatment	6/25/04	624, 625
65283	Aqueous	SP10, Effluent from wastewater treatment	6/22/04	624, 625
65285	Aqueous	SP10, Effluent from wastewater treatment	6/23/04	624
65289	Aqueous	SP10, Effluent from wastewater treatment	6/25/04	625

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EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65291	Solid	SP11, Screening Solids	6/22/04	624, 625
65292	Solid	SP12, Biosludge Waste	6/21/04	624, 625
65293	Solid	SP13, Incinerator Ash	6/21/04	625
65295	Aqueous	SP15, Source water	6/21/04	624, 625
65300	Aqueous	SP16,Trip Blank	6/03/04	624
65301	Aqueous	SP17, Equipment Blank	6/20/04	625

These data have been reviewed in accordance with SCC's General Data Review Guidelines for Organics Methods (Draft, October 2004) and according to the specifications in the methods. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary tables (Table 2 and 3).

SUMMARY

Method 625 samples were extracted and analyzed within the method-specified holding times, and GPC clean-up procedures were performed on all samples. Method 624 samples were prepared and analyzed within holding times, with the exception detailed below and in the data review summary table (Table 2). All calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for each analysis detected no contamination above the laboratory's reporting limits. The QC samples, including the ongoing and precision recovery samples (OPR), and MS/MSD samples; as well as surrogate and internal standard recoveries, demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below.

DATA ISSUES: METHOD 624

Holding Times

EPA sample 65223 was diluted and reanalyzed for tetrachloroethene because the result in the neat analysis exceeded the calibration range. The dilution was analyzed one day outside of the method-specified holding time. Therefore, the tetrachloroethene result in sample 65223 should be considered a minimum value.

Some of the other samples in this episode required dilutions for tetrachloroethene. The laboratory narrative pointed out that samples 65261 and 65273 were analyzed immediately following two samples that were high in tetrachloroethene, sample 65219 (440 µg/L tetrachloroethene) and sample 65231 (1400 µg/L tetrachloroethene). Since reanalyses were not performed for samples 65261 or 65273, it is unclear whether or not the concentration of tetrachloroethene in either sample was affected by carry-over from the previous samples. Other sample data were examined for similar instances and it was found that sample 65295, which yielded a non-detect for tetrachloroethene, was run immediately following sample 65292, that contained 190 µg/L of tetrachloroethene. Although no carry-over occurred in this instance, since the concentrations of tetrachloroethene in samples 65219 and 65231 were significantly higher than the 190 µg/L found in sample 65292, the possibility of carry-over cannot be ruled out. Therefore, SCC considers the tetrachloroethene results in samples 65261 and 65273 to be estimated values.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples

According to the scheduling facsimile, the MS/MSD samples were to be prepared and analyzed at the rate of one MS/MSD per every ten samples (double the method-specified frequency of 5%). For the volatiles analysis, MS/MSD aliquots were provided for samples 65265 and 65269. Due to a laboratory oversight, however, the MS/MSD for sample 65269 was not analyzed. SCC was not aware of this oversight until the data review was performed. By that time, the holding time for the samples had long expired, and therefore, SCC decided not to request that the laboratory prepare and analyze the MS/MSD. As a result, there are no MS/MSD data with which to evaluate the effect of the sample matrix on this specific sample. However, both samples are wastewater effluents from the same sampling point and could be expected to behave similarly, such that the lack of the one of these MS/MSD pairs is not a serious omission.

DATA ISSUES: METHOD 625

Ongoing Precision and Recovery (OPR)

Benzidine was either not recovered, or had very low percent recoveries, in the OPRs associated with samples in this episode. Although Method 625 does not provide QC limits for benzidine recovery, the lack of recovery in the OPRs indicates potential difficulties in the extraction of this compound in samples. Given this, and the fact that the recovery of benzidine has historically been problematic, SCC recommends that the benzidine results in all samples be excluded from the database (see Table 3).

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

An MS/MSD sample was prepared for solid sample 65293. Several analytes had recoveries that were either below the method-specified criteria, or were not recovered in the MS/MSD. Although Method 625 does not provide QC limits for some of these analytes, the low recoveries indicate the presence of matrix interference in this sample. Therefore, for analytes with low recoveries in the MS/MSD, SCC considers the results for these compounds in this sample to be of acceptable quality, but they may be minimum values. For analytes not recovered in the MS/MSD, SCC recommends that the results be excluded from the database. These instances are detailed in the data review summary table (Table 3).

TECHNICAL NOTES :

Reporting Limits

The reporting limits for this project are the same limits required for Methods 1624 and 1625, and are based on the lowest initial calibration standard, adjusted for sample size and dilution.

The laboratory increased the QC spiking concentrations and the minimum level (ML) for 2-chloroethyl-vinyl ether in the Method 624 by a factor of five because of problems with sensitivity for this analyte. The increased ML for this analyte is reflected in the database.

Sample Reporting

Due to a reporting error, the laboratory reported sample 65285 as sample 65284. The database has been corrected to reflect the actual sample number.

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's data review team leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2 - Data Review Summary Table for Method 624

Episode: 6503 **Analysis:** Method 624

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
65223	Tetrachloroethene	Acceptable quality, but may be minimum value	Holding time exceeded	NA	270 µg/L
65261 65273	Tetrachloroethene	Estimated values	Potential carry-over from previous sample analysis	NA	10 µg/L 27 µg/L

Table 3 -Data Review Summary Table for Method 625

Episode: 6503 **Analysis:** Method 625

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
All samples	Benzidine	Exclude from database	No OPR % recoveries	Exclude	NA
65293	2-Nitrophenol, 2,4,6-Trichloro-phenol	Acceptable quality, but may be minimum value	Low MS/MSD % recoveries	NA	ND
65293	4-Nitrophenol, Pentachlorophenol, Hexachlorocyclo-pentadiene	Exclude from database	No MS/MSD % recoveries	Exclude	NA

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MEMORANDUM

DATE: December 14, 2004

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for PCB Congeners Analyses for the Alaskan Cruise Ship Industry
Episode 6503

OVERVIEW

Under EPA Purchase Order EP-C-04-047, Axys Analytical Services submitted data for the analysis of chlorinated biphenyl congeners by EPA Method 1668A for one sample in Episode 6503. Table 1 provides a complete listing of the sample, matrix, sample description, and the required analytical method.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6503	65219	Aqueous	SP6, Influent Wastewater	6/24/04	1668A

These data have been reviewed in accordance with SCC's Data Review Guidelines for Chlorinated Biphenyl Analysis (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with this sample. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

The sample was successfully extracted and analyzed for the target analytes in EPA Method 1668A within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks associated with this sample detected no contamination above the laboratory's reporting limits. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable, with the clarification provided below.

Reporting Limits

The laboratory's reporting limits are at the method-specified minimum levels (MLs). The sample was extracted using a 910-mL aliquot, rather than the method-specified 1000-mL aliquot, due to volume constraints. This variation in sample size increased the MLs for sample 65219 by 10%. As reported by the laboratory, the MLs provided in the database for this sample reflect the smaller sample volume.

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Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

If you have any questions regarding the analyses of this sample or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

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MEMORANDUM

DATE: December 16, 2004

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for Pesticide Analyses for the Alaskan Cruise Ship Industry, Episode 6503

OVERVIEW

This data review narrative supersedes the original narrative dated November 5, 2004. At EPA's request, a GC/MS analysis was conducted on sample 65227 because of the concern about potential false positive results for propachlor and simazine from the initial GC analysis. The presence of these two pesticides was not confirmed by GC/MS analysis. Therefore, the EAD database has been revised to report propachlor and simazine as non-detects for sample 65227. The revisions contained in this narrative are in **boldface.**

Under EPA Purchase Order EP-C-04-046, Pacific Analytical, Inc. (PAI) submitted data for the analysis of organohalide pesticides by EPA Method 1656A and organophosphorus pesticides by EPA Method 1657A for five samples in Episode 6503. Table 1 provides a list of samples, matrices, descriptions, and the required analytical methods.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Method (s)
65215	Aqueous	SP5, Galley wastewater	6/22/04	1656A, 1657A
65227	Aqueous	SP6, Influent to wastewater treatment	6/22/04	1656A
65240	Aqueous	SP7, Influent to wastewater treatment	6/23/04	1656A
65223	Aqueous	SP6, Influent to wastewater treatment	6/22/04	1657A
65239	Aqueous	SP7, Influent to wastewater treatment	6/22/04	1657A

These data have been reviewed in accordance with SCC's Data Review Guidelines for Pesticide Analyses (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary tables (Tables 2A and 2B).

SUMMARY

All samples were successfully extracted and analyzed for the target analytes in EPA Methods 1656A and 1657A within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for each analysis detected no contamination above the laboratory's reporting limits. All organohalide pesticides samples were processed through gel

6101 Stevenson Avenue
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703.461.2000 Fax 703.461.2020

permeation chromatography (GPC), Florisil, and sulfur removal cleanups. All organophosphorus pesticides samples were processed through GPC and carbon column cleanup. The QC samples, including the ongoing precision and recovery sample (OPR) and the matrix spike/matrix spike duplicate (MS/MSD) samples, demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below.

Reporting Limits

The laboratory's reporting limits are based on the lowest calibration points specified in the methods, adjusted for dilution, rather than the minimum levels (MLs) listed in the methods. In most cases, the laboratory's reporting limits are lower than the method-specified MLs.

Some sample results in this episode were reported by the laboratory with a "J" flag, which indicates an estimated result that is below the laboratory's reporting limit. In keeping with current EAD practices, and to maintain consistency, all "J" flagged data will be reported in the database as non-detects at the laboratory's reporting limits.

Multiple Qualifiers

Some analytical results were affected by multiple qualifiers. In cases where these qualifiers suggest different biases, SCC considers the data to be estimated values. The effect of each QC failure and its associated qualifier are described in this data review narrative. Where multiple QC failures occur, the cumulative effects of the associated qualifiers are documented in the Tables 2A and 2B.

DATA ISSUES: METHOD 1656A

Ongoing Precision and Recovery (OPR)

Ethalfluralin, benfluralin, dichlone, and carbophenothion were recovered below the method-specified criteria in the OPRs associated with samples 65215, 65227, and 65240. Therefore, SCC considers the non-detect data in these samples to be of acceptable quality, but they may be minimum values. See Table 2A.

Norflurazon was not recovered in the OPR associated with all samples in this episode. Because it cannot be ascertained whether or not this analyte would have been detected if present in the samples, SCC recommends excluding norflurazon data from the database for these samples. See Table 2A

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

MS/MSD samples were prepared for sample 65227. Dichlone was recovered below the method-specified criteria. Therefore, SCC considers the non-detect dichlone data in this sample to be of acceptable quality, but it may be a minimum value. For captan and bromacil, the relative percent difference (RPD) between MS/MSD exceeded criteria, but these analytes were not detected in the sample. Therefore, SCC believes that the data quality is not affected.

Acephate was not recovered in the MS/MSD samples. This analyte also was not detected in any of the samples in this episode. Therefore, because it cannot be ascertained whether or not this analyte would have been detected if present in the sample, SCC recommends excluding acephate data from the database for sample 65227. See Table 2A.

Sample Results

According to the GC method, the computed result for a target analyte detected on the primary column analysis must be confirmed and agree within a factor of two with the result computed for that analyte on the confirmation column. For sample 65227, the propachlor result of 0.163 µg/L from the primary column differed by more than the method-specified factor of two from the confirmation column result of 3.27 µg/L, suggesting that a positive interference may be present.

Due to possible matrix interferences in sample 65227, the chromatograms from both primary and secondary columns show that the simazine peak, although distinct, is not completely resolved from other closely eluting compounds. Because other compounds elute within 20 seconds on the primary column, and non-target multi-component peaks surround the simazine peak on secondary column, the simazine identification and quantification are suspect.

After discussions with SCC, EPA authorized the analysis of sample 65227 by a GC/MS method utilizing selected ion monitoring (SIM) to determine if propachlor and simazine were, in fact, present in the samples, or if the original GC/ECD results were false positives. The results of the GC/MS SIM analysis were subsequently reviewed by SCC and the presence of these two pesticides could not be confirmed. Therefore, the EAD database has been revised to report propachlor and simazine as non-detects for sample 65227.

For sample 65240, kepone could not be confirmed on a secondary column because kepone does not elute on the ZB-1701 column used for confirmation. In addition, the chromatogram from the primary column showed poor baseline integration due to matrix interferences, which could lead to a false positive result. Without further efforts to confirm the results, it cannot be ascertained whether or not this analyte is present in the sample. Given the relatively low kepone concentration of 1.62 µg/L, it is likely that confirmation would require analysis by high resolution GC/MS. Considering the fact that kepone has not been manufactured or registered for use in the U.S. for many years, it seems unlikely that the peak tentatively identified as kepone during this analysis is actually kepone. **After consultation with SCC, EPA decided that high resolution GC/MS confirmation of this sample was not warranted.** Therefore, SCC recommends excluding kepone data from the database for sample 65240 due to a severe matrix interference (See Table 2A).

Surrogate Recoveries

For samples 65215 and 65227, the surrogate recoveries for decachlorobiphenyl on both columns are below the method-specified criteria due to matrix interferences. However, the other two surrogate recoveries are within the method-specified criteria, indicating that the extraction efficiency is in control. Therefore, SCC believes that the data quality for these samples is not affected by the low recovery of one surrogate.

DATA ISSUES: METHOD 1657A

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

MS/MSD samples were prepared for sample 65223. TEPP was recovered below the method-specified criteria. Therefore, SCC considers the non-detect value for TEPP data in this sample to be of acceptable quality, but it may be a minimum value. See Table 2B.

Surrogate Recoveries

For sample 65239, the surrogate recoveries for triphenylphosphate on both columns are below the method-specified criteria. However, the other surrogate recovery is within the method-specified criteria indicating that the extraction efficiency is in control. Therefore, SCC believes that the data quality for this sample is not affected by the low recovery. None of the organophosphorus pesticides were detected in any of the samples in this episode.

Technical Notes

Kepone was detected in the preparation blank associated with the samples in this episode at 0.322 μg/L, which was below the laboratory's reporting limit. However, the presence of kepone in the blank does not adversely affect the data for samples 65215 and 65227, because, kepone was not detected above the laboratory's reporting limit in these samples. For sample 65240, kepone data was excluded from the database, as described above.

If you have any questions regarding the analyses of these samples or the review of these data, please contact me by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2A
Data Review Summary Table

Episode: 6503 **Analysis:** 1656A

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analytes	Action	Reason	SCC Qual	Level
65240	kepone	Exclude from database	Result is not confirmable on second column analysis; severe matrix interference	Exclude	NA
65215, 65240	ethalfluralin, benfluralin, dichlone, carbophenothion	Acceptable quality, but may be minimum values	Low OPR % recoveries	NA	ND
65227	ethalfluralin, benfluralin, carbophenothion	Acceptable quality, but may be minimum value	Low OPR % recoveries	NA	ND
65227	dichlone	Acceptable quality, but may be minimum value	Low OPR % recovery; low MS/MSD % recoveries	NA	ND
65227	**propachlor, simazine**	**Include in database as non-detects**	**Analytes not confirmed in GC/MS analysis**	**NA**	**ND**
65215, 65227, 65240	norflurazon	Exclude from database	No OPR % recoveries	Exclude	NA
65227	acephate	Exclude from database	No MS/MSD % recoveries	Exclude	NA

ND = Non-detect at the laboratory's reporting limit. See level in database.
NA = Not applicable

Table 2B
Data Review Summary Table

Episode: 6503 **Analysis:** 1657A

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65223	TEPP	Acceptable quality, but may be minimum value	Low MS/MSD % recoveries	NA	ND

ND = Non-detect at the laboratory's reporting limit. See level in database.
NA = Not applicable

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6503

Data Validation Report For Settleable Solids Samples

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

December 13, 2004

Settleable Solids Method 160.5

Completeness

During Sampling Episode 6503, a total of 19 samples (excluding QC samples) were collected for analysis of settleable solids (SS) by EPA Method 160.5. All 19 samples received by the laboratory were analyzed for SS for a completeness of 100% (all planned samples were collected and analyzed). The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete SS data for the samples listed in Table 1.

Table 1. SS Samples Collected During Sampling Episode 6503

Sample Numbers	Sample Point Description
65219, 65223, 65227, 65231, 65235	Treatment System Influent
65261, 65265, 65269, 65273, 65277, 65287, 65289	Treatment System Effluent
65207	Accommodations
65215	Galley
65202	Laundry
65211	Food Pulper
65291	Screening Solids
65292	Waste Biosludge
65295	Source Water

Holding Times

Method 160.5 requires SS samples be analyzed within 48 hours following collection. Analysis of traffic reports and laboratory data sheets indicates five samples were analyzed outside the 48 hour holding time. Table 2 provides information on the samples analyzed outside the method-specified holding time.

Table 2. SS Samples Exceeding Hold Times

Sample Number	Sample Description	Sample Hold Time	Method Hold Time	SS Result
65235	Treatment System Influent	54.2 hours	48 hours	69 ml/L
65277	Treatment System Effluent	54.2 hours	48 hours	1.0 ml/L

Sample Number	Sample Description	Sample Hold Time	Method Hold Time	SS Result
65289	Treatment System Effluent	54.2 hours	48 hours	< 0.11 ml/L
65287	Treatment System Effluent	78 hours	48 hours	<0.11 ml/L
65207	Accommodations	84 hours	48 hours	2.1 ml/L

To determine the impact of exceeding the holding times for these five samples, results of similar samples were reviewed. Table 3 shows the SS results for treatment system influent and effluent samples that were analyzed within the 48 hour holding time. The data in Table 3 show the SS concentrations measured in the influent to the treatment system ranged from 22 to 82 ml/L. The SS concentration measured in the effluent from the treatment system ranged from <0.11 to <0.13 ml/L.

Table 3. SS Results for Samples Analyzed within the 48 Hour Holding Time

Sample Number	Sample Description	SS Concentration (ml/L)
65227	Treatment System Influent	22
65231	Treatment System Influent	66
65219	Treatment System Influent	40
65223	Treatment System Influent	82
65265	Treatment System Effluent	<0.13
65269	Treatment System Effluent	<0.11
65273	Treatment System Effluent	<0.11
65261	Treatment System Effluent	<0.11

The SS concentration measured on treatment system influent sample 65235, analyzed outside the 48-hour holding time, was 69 mL/L, which falls within the range of SS concentrations for the influent samples analyzed within the holding times shown in Table 3. The SS concentrations for treatment system effluent samples 65287 and 65289, analyzed outside the 48-hour holding time, were reported as below the detection limit of 0.11 mL/L. The four other effluent samples in this episode that were analyzed within the holding time were also reported as non-detects at a similar level (see Table 3).

The remaining effluent sample analyzed outside of the 48-hour holding time, sample 65277, had a measured SS concentration of 1 mL/L, which is above the non-detect results for the effluent samples measured within holding time. The result for this sample may represent a maximum value.

Based on these comparisons, the SS results from samples 65235, 65277, 65289, and 65287 should be considered valid for the cruise ship rulemaking.

The SS result from the accommodations wastewater sample, 65207, can not be compared to similar data within the data set since only a single accommodations wastewater sample was collected. Although the accommodations wastewater is a component of the treatment system influent, this sample was held longer than any other sample (influent or effluent) in this episode. Therefore, because there is no direct basis for comparison with similar samples analyzed within the holding time, the result for sample 65207 should be considered an estimated value.

Precision Analysis

Reproducibility for SS is measured as relative percent difference (RPD) between duplicate samples. The QAPP for the Cruse Ship Rulemaking specifies the target RPD for field duplicate samples as less than 30%. Field duplicate samples were collected for SS, and the results are shown in Table 4. The RPDs shown in Table 4 could not be calculated since one or both of the field duplicate sample results were less than the laboratory reported detection limit. Although the RPD for these samples cannot be calculated, SS analysis precision is acceptable for this program, and the reported SS results are valid.

Table 4. Relative Percent Difference Between Field Duplicate Samples

Sample No.	SS Result	Sample No	SS Result	RPD	RPD Target
65273	<0.11 ml/L	65287	<0.11ml/L	NA	<30%
65277	1.0 ml/L	65289	<0.11 ml/L	NA	<30%

NA: RPD cannot be calculated since one or both of the sample results is less than the detection limit.
RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.

Data Quality Assessment

This data validation assessment indicates the SS data collected during Sampling Episode 6503 can be used for the large cruise ship rulemaking effort.

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MEMORANDUM

DATE: January 10, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for Available Cyanide Analyses by Method OIA-1677 for the Alaska Cruise Ship Industry, Episode 6503

OVERVIEW

Under EPA Purchase Order EP-C-04-048, Bayer Material Science LLC, submitted available cyanide data by EPA Method OIA-1677 for 19 samples in Episode 6503. Table 1 provides a complete listing of samples and matrices. Available cyanide was the only analysis performed by Bayer for these samples.

Table 1 - Sample Identifiers, Descriptions, and Sampling Dates

EPA Sample #	Matrix	Sample Description	Sampling Date
65202	Aqueous	SP1, Laundry wastewater	6/23/04
65207	Aqueous	SP3, Accommodations wastewater	6/24/04
65211	Aqueous	SP4, Food pulper wastewater	6/22/04
65215	Aqueous	SP5, Galley wastewater	6/22/04
65219	Aqueous	SP6, Influent to wastewater treatment	6/21/04
65223	Aqueous	SP6, Influent to wastewater treatment	6/22/04
65227	Aqueous	SP6, Influent to wastewater treatment	6/23/04
65231	Aqueous	SP6, Influent to wastewater treatment	6/23/04
65235	Aqueous	SP6, Influent to wastewater treatment	6/25/04
65261	Aqueous	SP9, Effluent from wastewater treatment	6/21/04
65265	Aqueous	SP9, Effluent from wastewater treatment	6/22/04
65269	Aqueous	SP9, Effluent from wastewater treatment	6/23/04
65273	Aqueous	SP9, Effluent from wastewater treatment	6/23/04
65277	Aqueous	SP9, Effluent from wastewater treatment	6/24/04
65281	Aqueous	SP10, Effluent from wastewater treatment	6/21/04
65283	Aqueous	SP10, Effluent from wastewater treatment	6/23/04
65291	Solid	SP11, Screening solid	6/22/04
65292	Sludge	SP12, Waste biosludge (desludge)	6/22/04
65295	Aqueous	SP15, Source water	6/21/04

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

These data have been reviewed in accordance with SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004), and with the specifications listed in the analytical requirements summary for this episode. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary table (Table 2).

SUMMARY

All samples were successfully analyzed within the method-specified holding times for available cyanide. Initial precision and recovery samples (IPRs) were successfully performed prior to sample analysis. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks were performed and there was no contamination detected above the laboratory reporting limits. The QC samples, including the ongoing and precision recovery sample (OPR) and matrix spike/matrix spike duplicate (MS/MSD) samples, demonstrated that laboratory performance for these analyses was acceptable, with the exception of the data issues described below.

DATA ISSUES: AVAILABLE CYANIDE GREATER THAN TOTAL CYANIDE

Sample Results

For all samples in this episode, SCC evaluated total cyanide results against available cyanide results, and found that available cyanide was detected in samples 65207, 65219, 65227, 65231, 65235, 65265, 65281, and 65295, while total cyanide were not detected in these samples. In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. However, for these samples, it is important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the available cyanide determination was performed by a different laboratory. In addition, the overall homogeneity of the waste stream being sampled can have a significant effect on the cyanide results. Therefore, it may not be possible to identify problems that would invalidate one cyanide fraction or the other.

A review of the traffic reports (TRs) for the samples indicates that some of the samples in Episode 6503 were not treated with lead carbonate to remove sulfides. SCC consulted EPA and the sampling contractor and determined that the following 11 samples were not treated with lead carbonate:

65202, 65207, 65211, 65227, 65231, 65235, 65269, 65273, 65277, 65283, and 65295

The total cyanide result for Sample 65273 (effluent) was reported as a non-detect at 5 µg/L and available cyanide was a non-detect at 2 µg/L. An MS/MSD pair for available cyanide was prepared from this sample and had recoveries of 101% and 102% respectively, while the MS/MSD recoveries for total cyanide were 5% and 1%, as noted earlier. This suggests a significant potential for low bias in the total cyanide result. Therefore, based on the low MS/MSD recoveries for total cyanide in this sample, the total cyanide non-detect is considered a minimum value and the available cyanide result is considered acceptable without qualification.

There were nine other samples in Episode 6503 that exhibited the pattern of total cyanide results less than the available cyanide results. Samples 65219, 65227, 65231, and 65235 are influents to treatment and, as noted above, there are no MS/MSD analyses that demonstrate the performance of either method for this matrix type. Samples 65227, 65231, and 65235 also are among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and given the potential for positive

interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for samples 65227, 65231, and 65235 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples. Sample 65219 was treated in the field, therefore SCC recommends including both cyanide results for sample 65219 in the database, but flagging them to indicate the irreconcilable differences.

The total cyanide results for Sample 65207 (accommodations wastewater) were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 15.7 µg/L. The MS/MSD recoveries for total cyanide were 21% and 22%. Sample 65207 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, given the low MS/MSD recoveries for total cyanide in this sample and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65207 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65211 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Total cyanide was detected at 14 µg/L, while available cyanide was reported at 88.4 µg/L. Sample 65211 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65211 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65295 is listed as a source water sample, a matrix type that should not present significant analytical difficulties. Sulfide was not detected in this sample by the field test performed at the time of collection and therefore, this sample is among the 11 samples that were not treated with lead carbonate. Although the presence of available cyanide at 19 µg/L in the source water is unexpected, there is no analytical evidence to suggest that the available cyanide result be excluded. However, an engineering review or other information not available to SCC may lead to a different conclusion. Therefore, SCC recommends including both cyanide results for sample 65295 in the database, but flagging them to indicate the irreconcilable differences.

Episode 6503 included two sets of field duplicate samples that were sent to the laboratories blind. SCC does not normally evaluate the agreement between field duplicate samples. However, because of concerns about the cyanide data, at EPA's request, SCC obtained information about the field duplicates from the sampling contractor and performed some simple comparisons. The two field duplicate pairs were samples 65261 and 65281, and samples 65265 and 65283, all effluent samples. The total cyanide results in sample 65261 were reported as a non-detect at 5 µg/L, while available cyanide was reported as a non-detect at 2 µg/L. For sample 65281, the blind field duplicate, the total cyanide results were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 8.96 µg/L. A similar pattern occurs for the cyanide results in the other field duplicate pair. Total cyanide was reported as a non-detect at 5 µg/L in both samples 65265 and 65283, while available cyanide was detected at 5.86 µg/L in sample 65265 and as a non-detect a 2 µg/L in sample 65283.

The MS/MSD recoveries for total cyanide in effluent sample 65273 were very low (1% and 5%), and low (33% and 30%) in sample 65269, suggesting a potential negative basis that may affect the total cyanide results in samples 65261, 65281, 65265, and 65283. Therefore, SCC recommends that the total cyanide results in sample 65261 and 65281 be considered minimum values. The difference between the available cyanide results in the two field duplicate samples (e.g., a non-detect at 2 µg/L and a detect at 8.96 µg/L) cannot be explained on the basis of the MS/MSD results for available cyanide in sample 65273, which was also an effluent. Given the discrepancy between the field duplicate results for available cyanide,

SCC recommends including the available cyanide results for samples 65261 and 65281 in the database, but flagging them to indicate the irreconcilable differences. SCC recommends that the total cyanide results for samples 65261 and 65281 also be flagged to indicate the irreconcilable differences, as a further precaution.

Because of the low MS/MSD recoveries in the other effluent samples, the total cyanide result for sample 65265 is considered a minimum value. The available cyanide result of 5.86 µg/L is well within 30% of the reported detection limit for total cyanide (e.g., 5 µg/L), and therefore would normally not be qualified. However, because the available cyanide result in the field duplicate of the sample, 65283 is a non-detect at 2 µg/L, SCC recommends including both the total and available cyanide results for sample 65265 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65283 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Given the very low MS/MSD recoveries for total cyanide in effluent samples in this episode, SCC recommends flagging both cyanide results for sample 65283 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples.

Please note that the samples were analyzed for total cyanide by Analytical Laboratory Services, Inc. A separate narrative has been prepared for the total cyanide analysis.

TECHNICAL NOTES:

Reporting Limits

The laboratory reported sample results down to the method detection limit (MDL), rather than the method-specified minimum level (ML). In keeping with current SCC practices, and in order to maintain consistency in the database, the reporting limits for available cyanide have been adjusted in the database to reflect the method-specified ML of 2.0 µg/L.

If you have any questions regarding the analysis of these samples or the review of these data, please contact me at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6503 **Analysis:** Available Cyanide

Industry: Alaska Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65207, 65211	Available cyanide	—	Sample not treated with lead carbonate to remove sulfides. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.	MISCA	NA
65219		—	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.	IRR	NA
65227, 65231, 65235		—	Samples not treated with lead carbonate to remove sulfides. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.	MISCA	NA
65261, 65265, 65281		—	Based on field duplicate results, irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.	IRR	NA
65283		—	Sample not treated with lead carbonate to remove sulfides. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.	MISCA	NA
65295		—	Irreconcilable results for total and available cyanide.	IRR	NA

NA = Not applicable
IRR = Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
MISCA = Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: January 18, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Harry B. McCarty
Senior Scientist

SUBJECT: Issues Associated with Results for Total Cyanide versus Available Cyanide for Episodes 6503, 6504, 6505, and 6506

The purpose of this memorandum is to provide a general discussion of the analysis of various forms of cyanide in aqueous samples, describe the cyanide analyses conducted as part of EPA's investigation of discharges from Alaskan cruise ships, and provide recommendations regarding specific results from Sampling Episodes 6503, 6504, 6505, and 6506.

Forms of Cyanide

Cyanide is an inorganic moiety composed of one carbon atom and one nitrogen atom that is most often found as an anion with a charge of -1. The cyanide anion can bond with various metals or other elements to form a wide range of cyanide compounds. The simplest form of cyanide is hydrogen cyanide, HCN, which readily dissociates into H^+ and CN^- in water. HCN is known as "free cyanide" and is the most toxic form of cyanide. Most forms of cyanide are toxic, with their toxicities depending on their ability to release free cyanide.

"Total cyanide" (or "cyanide, total") is an operationally defined term used to describe the cyanides that are measured using the total cyanide test. Total cyanide methods attempt to measure the amount of CN^- present in a sample, regardless of its oxidation state or complexation to other ions or compounds. Some complexes and organic cyanide compounds are resistant to the dissociation that occurs during the digestion/distillation step, and others are completely decomposed. Therefore, total cyanide is a method-defined parameter because the analytical conditions determine the actual analyte quantity measured.

Compounds such as metallocyanides are resistant to oxidation, with iron cyanide being one of the most resistant, and nickel, copper, and noble metal cyanides being somewhat resistant. These compounds will contribute to the measured total cyanide to some degree, but are not always completely recovered by the digestion/distillation procedure. Cyanide compounds such as thiocyanate, cobaltocyanide compounds, and cyanohydrin organic compounds are not measured at all by this procedure include because they decompose during the digestion procedure.

Two other operationally defined groups of cyanide species are "available cyanide," and "cyanide amenable to chlorination" (or "amenable cyanide"). Available cyanide generally encompasses both the free cyanide and those complexed species that are relatively easily dissociated in a weak acid solution. Amenable cyanide is the term used to describe that fraction of cyanide that can be destroyed by the common wastewater treatment procedure of chlorinating the wastewater. Some cyanides in solution will react with chlorine (Cl_2) to form cyanogen chloride (CNCl), a highly toxic gas with limited solubility. The cyanogen chloride hydrolyzes at alkaline pH to form the cyanate ion (CNO^-), which is much less toxic than the parent cyanide. Amenable cyanide encompasses the true free cyanide portion, plus additional cyanides that easily dissociate in aqueous solutions.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Analytical Methods for the Analysis of Cyanide in Aqueous Samples

Total Cyanide Methods

The seven methods approved at 40 CFR 136 for total cyanide in aqueous samples are:

- EPA Method 335.2
- EPA Method 335.3
- Standard Method 4500-CN^- D
- Standard Method 4500-CN^- E
- ASTM Method D2036-98A
- USGS Method I-3300-85
- USGS Method I-4302-85

EPA Methods 335.2 and 335.3 were employed by the two laboratories that analyzed samples from Episodes 6503, 6504, 6505, and 6506 for total cyanide. However, this general discussion applies to all seven approved methods.

All of the total cyanide methods involve digestion of the sample using concentrated sulfuric acid with magnesium ion in solution as a catalyst. (The digestion procedure is presented as the stand-alone procedure Standard Method 4500-CN^- C). The cyanide is converted to HCN gas, which is collected in a scrubber containing NaOH. This solution is then analyzed for the CN^- ion. The determinative methods use one of several techniques to measure CN^-, including titration with silver nitrate, colorimetry with an organic dye, or automated distillation-colorimetry for continuous flow analytical systems that utilizes UV oxidation of the sample to release bound cyanide.

Available Cyanide Methods

The four methods approved at 40 CFR 136 for available cyanide in aqueous samples are:

- EPA Method 335.1
- Standard Method 4500-CN^- G
- ASTM Method D2036-98B
- Method OIA-1677

Method OIA-1667 was employed for the analyses of available cyanide in Episodes 6503, 6504, 6505, and 6506. However, this general discussion applies to all four approved methods.

Although these four methods are approved at 40 CFR 136 for “available cyanide,” there are slight differences in forms of cyanide that are targeted by these methods. Generally speaking, the differences are not significant in compliance monitoring, but may be more important in other types of investigations.

The OIA-1677 procedure targets the weak acid dissociable cyanide by treating the sample with ligand-exchange reagents that release cyanide ions from the metal-cyano complexes. During the analysis, cyanide ions are converted to hydrogen cyanide (HCN) that passes through a gas diffusion membrane into an alkaline receiving solution where it is converted back to cyanide ion. The cyanide ion is monitored amperometrically, using a silver electrode.

EPA Method 335.1, SM 4500-CN^- G, and ASTM D2036-98B measure the cyanide amenable to chlorination. In these methods, two aliquots of the sample are analyzed. One aliquot is subjected to chlorination and the other aliquot is not. Both aliquots are distilled and analyzed for CN^-. The amenable

cyanide is calculated as the difference between the cyanide results from the chlorinated and nonchlorinated aliquots.

Difficulties and Interferences in the Analysis of Cyanide

A number of interferences affect cyanide determinations. Strong oxidizers, such as free chlorine, will destroy the "amenable" portion of cyanide. Sulfide present in the sample will oxidize cyanide into thiocyanate, which is not measurable in the cyanide methods. The sample should be tested for sulfide at the time of sample collection, and if sulfides are found, they should be removed by precipitation with lead carbonate or cadmium nitrate. This precipitation procedure should take place before the sample is preserved with NaOH, and any insoluble sulfide that is produced should be removed by filtration. Additional steps may be needed if the sample contains sulfide *and* particulate matter that may consist of alkali metal-heavy metal-cyanide complexes.

Most interferences in the total cyanide determination are removed by the distillation step, but some are not. Nitrate and nitrite can form cyanide as a reduction product of nitrogen-containing organic compounds, and are removed by the addition of sulfamic acid during distillation. Aldehydes can form cyanohydrins, which will convert to nitrile during the digestion. Sulfides also can be produced during distillation, and will distill along with cyanide and form thiocyanate. Sulfide production can be prevented by the addition of lead carbonate to the absorber solution, and the subsequent filtration of the absorber solution before analysis. Other potential interferences include sugars that can form cyanohydrins, sulfur compounds that may release sulfide, compounds that could release or form nitrite, as well as any sample constituent that could produce one of the interferences under the conditions of the digestion.

Method OIA-1677 does not employ a digestion step. Therefore, sulfides must be removed by the precipitation procedure described above. In addition to concerns about sulfides reacting with the cyanide in the sample before it can be measured (i.e., a negative interference), sulfides also can be a positive interference in this procedure if they react with acid in the sample to produce hydrogen sulfide (HS_2). The hydrogen sulfide will cross the membrane in the gas diffusion cell and produce a signal at the silver electrode that would be measured as cyanide. As noted in the method, "polysulfides" (compounds containing more than one sulfide) can be intractable interferences.

Interpretation of Cyanide Results

In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. While this usually holds true for wastewater effluent samples, some effluents and some other sample types, such as influents, may yield results in which the free or available cyanide results exceed the total cyanide results. For example, the results for free cyanide derived using the chlorination technique can result in free cyanide concentrations greatly in excess of total cyanide concentrations. When this occurs, it is likely due to the formation of cyanide by chlorination of nitrogen-containing organic compounds in the sample. While it might be possible to determine if such nitrogen-containing organics were present in the sample, this step is neither required nor practical for laboratories performing routine cyanide analyses.

Sulfides that may be in the sample present a significant possibility for false negative results for total cyanide through the oxidization of cyanide to thiocyanate, which is not measured by the cyanide methods, as discussed above. Sulfides can be both a negative interference and a positive interference with the determination of available cyanide by Method OIA-1677, as described above.

It is also important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the amenable cyanide determination is made using

separate aliquots of a separate sample. Thus, the overall homogeneity of the waste stream being sampled can have a significant effect on the cyanide results.

While the results for any cyanide measurement are evaluated by SCC relative to the requirements of the methods used for the determinations, it may not be possible to identify problems that would invalidate one cyanide fraction or the other. In instances where there are one or more QC failures associated with one of the cyanide fractions, but not with the other fraction, the results for the fraction with the QC failures will be appropriately qualified.

In instances where there are no QC failures associated with either cyanide fraction, but the available cyanide results are greater than the total cyanide results by a large margin, there is no way to determine which analysis was correct. In such cases, both sets of cyanide results are suspect. For the purposes of reviewing results for EPA's Effluent Guidelines Program, when cyanide is reported as present (e.g., not a non-detect) in both fractions and there are no QC failures in either fraction, differences where the available cyanide results are more than 30% above the total cyanide results suggest that irreconcilable problems exist. The 30% difference is a consensus value used by SCC. Differences less than 30% are considered a function of the routine variability that could be present in both measurements.

When such irreconcilable problems exist with the results of paired samples analyzed for both total and available cyanide, SCC recommends that both results (total and available) be included in the database, and that both results be flagged to alert the data user to the presence of such problems.

Cyanide Methods Used for Samples from the Alaskan Cruise Ship Project

The following table lists the methods used for total and available cyanide for Episodes 6503, 6504, 6505, and 6506. Two different laboratories performed the total cyanide analyses for these four episodes, using two different methods approved at 40 CFR 136. One other laboratory analyzed the available cyanide for all four episodes using Method OIA-1677.

Episode #	Method for Total Cyanide	Method for Available Cyanide
6503	EPA Method 335.3	Method OIA-1677
6504	EPA Method 335.2	Method OIA-1677
6505	EPA Method 335.3	Method OIA-1677
6506	EPA Method 335.2	Method OIA-1677

Based on communications with the sampling contractor, the samples were tested for sulfide in the field, using a field colorimeter with a detection limit of approximately 10 µg/L. Samples testing positive for sulfides were treated in the field to minimize the interferences. Because of concerns regarding whether the treated samples were subsequently filtered in the field, the laboratories were instructed to filter any sample showing turbidity.

A review of the traffic reports (TRs) for the samples in these four episodes indicates that some of the samples in Episode 6503, the first episode in the Alaskan Cruise Ship project, were not treated with lead carbonate to remove sulfides. SCC consulted EPA and the sampling contractor and determined that the following 11 samples were not treated with lead carbonate:

65202, 65207, 65211, 65227, 65231, 65235, 65269, 65273, 65277, 65283, and 65295

In an effort to address the potential positive interference of nitrate and nitrite in the samples, the laboratories performing the total cyanide analyses were advised to increase the amount of sulfamic acid added to each sample during distillation by a factor of 2, from 2 g per sample to 4 g per sample.

Episode-specific Findings

SCC has reviewed the results for both total cyanide and available cyanide in Episodes 6503, 6504, 6505, and 6506. Episode-specific findings are detailed below.

In addition to the data qualifiers described in SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004), two additional qualifiers were developed to address the total and available cyanide results from the Alaskan Cruise Ship Project. In cases where the available cyanide results exceed those for total cyanide by more than 30% and there are not any matrix-specific quality control data such as matrix spike recoveries, the total cyanide and available cyanide results will be flagged with the "IRR" qualifier. The "SCC Reason" field in the database for such results will read "Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose."

In other instances, when SCC's review identifies multiple concerns with the results for a given sample, including those that begin with sample collection and others involving the analysis of the sample itself or any associated quality control samples, the total cyanide and available cyanide results will be flagged with the "MISCA" qualifier. The "SCC Reason" field in the database for such results will read "Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample."

Episode 6503

Three sets of matrix spike/matrix spike duplicate (MS/MSD) samples were prepared for total cyanide analysis in Episode 6503 on samples 65207 (accommodations wastewater), 65269 (an effluent), and 65273 (an effluent). The MS/MSD recoveries for the three aqueous MS/MSD pairs were below the acceptance limits:

- 22% and 21% for sample 65207,
- 30% and 33% for sample 65269, and
- 5% and 1% for sample 65273

suggesting a potential for low bias in the total cyanide results for the associated aqueous samples.

The recoveries for the laboratory control samples (LCS, OPR, or QC check sample) analyzed along with the field samples were acceptable, indicating that the laboratory's overall analytical process was in control and suggesting either problems with the distillation process or an interference present in the sample matrix. Because the focus of the EAD analytical contracts is on effluent samples and because there are no acceptance criteria for aqueous matrices other than effluents, no MS/MSD analyses were performed on samples representing influents to the treatment process.

The total cyanide result for Sample 65273 (effluent) was reported as a non-detect at 5 µg/L and available cyanide was a non-detect at 2 µg/L. An MS/MSD pair for available cyanide was prepared from this sample and had recoveries of 101% and 102% respectively, while the MS/MSD recoveries for total cyanide were 5% and 1%, as noted earlier. This suggests a significant potential for low bias in the total cyanide result. Therefore, based on the low MS/MSD recoveries for total cyanide in this sample, the total

cyanide non-detect is considered a minimum value and the available cyanide result is considered acceptable without qualification.

There were nine other samples in Episode 6503 that exhibited the pattern of total cyanide results less than the available cyanide results. Samples 65219, 65227, 65231, and 65235 are influents to treatment and, as noted above, there are no MS/MSD analyses that demonstrate the performance of either method for this matrix type. Samples 65227, 65231, and 65235 also are among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and given the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for samples 65227, 65231, and 65235 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples. Sample 65219 was treated in the field, therefore SCC recommends including both cyanide results for sample 65219 in the database, but flagging them to indicate the irreconcilable differences.

The total cyanide results for Sample 65207 (accommodations wastewater) were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 15.7 µg/L. The MS/MSD recoveries for total cyanide were 21% and 22%, as noted earlier. Sample 65207 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, given the low MS/MSD recoveries for total cyanide in this sample and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65207 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65211 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Total cyanide was detected at 14 µg/L, while available cyanide was reported at 88.4 µg/L. Sample 65211 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65211 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65295 is listed as a source water sample, a matrix type that should not present significant analytical difficulties. Sulfide was not detected in this sample by the field test performed at the time of collection and therefore, this sample is among the 11 samples that were not treated with lead carbonate. Although the presence of available cyanide at 19 µg/L in the source water is unexpected, there is no analytical evidence to suggest that the available cyanide result be excluded. However, an engineering review or other information not available to SCC may lead to a different conclusion. Therefore, SCC recommends including both cyanide results for sample 65295 in the database, but flagging them to indicate the irreconcilable differences.

Episode 6503 included two sets of field duplicate samples that were sent to the laboratories blind. The two pairs were samples 65261 and 65281, and samples 65265 and 65283, all effluent samples. The total cyanide results in sample 65261 were reported as a non-detect at 5 µg/L, while available cyanide was reported as a non-detect at 2 µg/L. For sample 65281, the blind field duplicate, the total cyanide results were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 8.96 µg/L. A similar pattern occurs for the cyanide results in the other field duplicate pair. Total cyanide was reported as a non-detect at 5 µg/L in both samples 65265 and 65283, while available cyanide was detected at 5.86 µg/L in sample 65265 and as a non-detect a 2 µg/L in sample 65283.

The MS/MSD recoveries for total cyanide in effluent sample 65273 were very low (1% and 5%), and low (33% and 30%) in sample 65269, suggesting a potential negative basis that may affect the total cyanide results in samples 65261, 65281, 65265, and 65283. Therefore, SCC recommends that the total cyanide results in sample 65261 and 65281 be considered minimum values. The difference between the available cyanide results in the two field duplicate samples (e.g., a non-detect at 2 µg/L and a detect at 8.96 µg/L) cannot be explained on the basis of the MS/MSD results for available cyanide in sample 65273, which was also an effluent. Given the discrepancy between the field duplicate results for available cyanide, SCC recommends including the available cyanide results for samples 65261 and 65281 in the database, but flagging them to indicate the irreconcilable differences. SCC recommends that the total cyanide results for samples 65261 and 65281 also be flagged to indicate the irreconcilable differences, as a further precaution.

Because of the low MS/MSD recoveries in the other effluent samples, the total cyanide result for sample 65265 is considered a minimum value. The available cyanide result of 5.86 µg/L is well within 30% of the reported detection limit for total cyanide (e.g., 5 µg/L), and therefore would normally not be qualified. However, because the available cyanide result in the field duplicate of the sample, 65283 is a non-detect at 2 µg/L, SCC recommends including both the total and available cyanide results for sample 65265 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65283 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Given the very low MS/MSD recoveries for total cyanide in effluent samples in this episode, SCC recommends flagging both cyanide results for sample 65283 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples.

Episode 6504

Three sets of MS/MSD samples were prepared for total cyanide analysis in Episode 6504 on samples 65519 (an effluent), 65523 (an effluent), and 65527 (accommodations wastewater), and all showed acceptable spike recoveries. Thus, there do not appear to be pervasive problems with the recovery of total cyanide in samples from this episode.

A comparison of the total cyanide results and available cyanide results for samples 65395, 65455, 65459, 65463, 65467, and 65471 indicates that the total cyanide results were non-detects at 5 µg/L, while available cyanide was detected in each of these samples at approximately 11 to 36 µg/L. In addition, total cyanide was reported as present in sample 65411 at 6 µg/L, while the available cyanide result was 35.7 µg/L (e.g., six time the total cyanide result).

Sample 65395 is listed as the galley wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65395 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65411 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system, and as noted above, there are no MS/MSD data that demonstrate method performance for matrices other than effluents. During the review of the data, SCC noted that the traffic report for the aliquot of Sample 65411 for total cyanide analysis indicated that the aliquot was collected at 14:00 on 8/10/04, while the traffic report for the aliquot submitted for available cyanide analysis indicated that that aliquot was collected at 3:00 PM (15:00) on 8/11/04. This concern was resolved following discussions with EPA and the sampling contractor, whose field records indicated that both aliquots were collected at the same time, and that the

one traffic report was incorrect. Having resolved the issue of the time of sample collection, but lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65411 in the database, but flagging them to indicate the irreconcilable differences.

Samples 65455, 65459, 65463, 65467, and 65471 are all influents to treatment, collected from the same sampling point on consecutive days. The results from samples 65463, 65467, and 65471 are remarkably consistent, varying by only 0.2 µg/L across all three samples. The results for samples 65455 and 65459 are similar to one another, but about twice the concentrations found in the other three samples from this sampling point. There are no MS/MSD analyses that demonstrate method performance for this matrix type, but the consistency in the results suggests that whatever matrix effects may be taking place, they are reproducible. However, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65455, 65459, 65463, 65467, and 65471 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6504, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Episode 6505

The data for total cyanide samples in Episode 6505 were delivered in five separate data packages, each with its own associated QC sample results. Six pairs of MS/MSD samples were prepared for total cyanide analyses in Episode 6505 on samples 65603 (galley wastewater), 65635 (accommodations wastewater), 65711 (an effluent), 65715 (an effluent), 65719 (an effluent), and 65741 (screening solids).

The data for a seventh pair of MS/MSD samples were delivered in the data package with the results for samples 65731 (galley wastewater) and 65745 (biosolids). However, because of limitations on the sample volume that was provided to the laboratory, the MS/MSD samples were prepared from a non-EPA sample of indeterminate origin and therefore are not useful in evaluating the performance of the total cyanide method on cruise ship samples.

Three of the MS/MSD pairs for aqueous samples and the one MS/MSD pair for the solid samples had acceptable recoveries of total cyanide. None of the samples used to prepare MS/MSD aliquots were samples where the available cyanide results exceeded the total cyanide results.

The MS/MSD results for sample 65603 (galley wastewater) showed recoveries of 59% in both aliquots, which is below the acceptance limits, and suggests a potential low bias in the total cyanide result for that sample. The available cyanide result of 2.2 µg/L is below the detection limit for the total cyanide analysis. Therefore, SCC recommends qualifying the total cyanide result as a minimum value and accepting the available cyanide result as reported.

Although MS/MSD samples were prepared from sample 65741 (screening solids) and met the acceptance criteria, there are no MS/MSD results for the biosolids matrix in this episode. This limits SCC's ability to evaluate the potential effects of the sample matrix for sample 65745 (biosolids), where the available cyanide results are almost 40% higher than the total cyanide results. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65745 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65731 is a galley wastewater. The only MS/MSD results for galley wastewater in this episode are for sample 65603, where the recoveries were below the acceptance criteria. Given the

potential for low bias in this matrix, SCC recommends qualifying the total cyanide result as a minimum value. SCC recommends including both cyanide results for sample 65731 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65659 is an influent sample and MS/MSD aliquots are not prepared for influents, as discussed earlier. Total cyanide was reported as not detected and the available cyanide was reported at 6 times the total cyanide detection limit. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65659 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6505, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Episode 6506

A comparison of the total cyanide results and available cyanide results for samples 65896, 65900, 65904, 65908, and 65912 indicates that the total cyanide results were non-detects at 5 µg/L, while available cyanide was detected in each of these samples at levels from approximately 36 to 77 µg/L.

All five of these samples are from the same sampling point, SP 2, and represent influents to the black water and gray water treatment system. Thus, these samples are not treated effluents. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65896, 65900, 65904, 65908, and 65912 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6506, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Summary of Results from Episodes 6503, 6504, 6505, and 6506

SCC's recommendations for handling the total and available cyanide results for the Alaskan Cruise Ship project samples are summarized in the table on the following page

Note: The results in the database are reported in the units provided by the laboratories that performed the analyses. Method OIA-1677 specifies reporting results in units of micrograms per liter (µg/L), whereas the older methods (335.2 and 335.3) specify reporting results in units of milligrams per liter (mg/L). However, for ease of comparison in the table the follows, the results for total cyanide have been converted to the same units as the available cyanide results, µg/L. "ND" indicates that cyanide was not detected. In these cases, the reported detection limit is shown in parentheses.

If you have any questions about the information in this memorandum or the cyanide results in the database, please do not hesitate to contact me at 703-461-2392, or by email at hmccarty@csc.com.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Jodi King, ERG
Deb Falatko, ERG
Deb Miller, CSC
Michael Walsh, CSC
Pornkeo Chinyavong, CSC

Summary of SCC Recommendations for Cyanide Results in the Alaskan Cruise Ship Project

Episode	Sample #	Matrix	Total Cyanide (µg/L)	Available Cyanide (µg/L)	SCC Recommendation
6503	65207	Accommodations wastewater	ND (5)	15.7	Sample not treated with lead carbonate to remove sulfides. Low MS/MSD recoveries for total cyanide. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65211	Food pulper wastewater	14	88.4	Samples not treated with lead carbonate to remove sulfides. No matrix-specific performance data. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65219	Influent to treatment	ND (5)	10.4	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65227	Influent to treatment	ND (5)	7.54	Samples not treated with lead carbonate to remove sulfides. No matrix-specific performance data for influents. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65231		ND (5)	35.4	
6503	65235		ND (5)	16	
6503	65261	Effluent from treatment	ND (5)	ND (2)	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65265		ND (5)	5.86	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65273		ND (5)	ND (2)	Total cyanide qualified as minimum value.
6503	65281		ND (5)	8.96	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65283	Effluent from treatment	ND (5)	ND (2)	Total cyanide qualified as minimum value. Sample not treated with lead carbonate to remove sulfides. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.

Episode	Sample #	Matrix	Total Cyanide (µg/L)	Available Cyanide (µg/L)	SCC Recommendation
6503	65295	Source water	ND (5)	19.1	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6504	65395	Galley wastewater	ND (5)	22.4	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6504	65411	Food pulper	6	35.7	
6504	65455	Influent to treatment	ND (5)	26.9	
6504	65459	Influent to treatment	ND (5)	29	
6504	65463	Influent to treatment	ND (5)	11.7	
6504	65467	Influent to treatment	ND (5)	11.5	
6504	65471	Influent to treatment	ND (5)	11.6	
6505	65603	Galley wastewater	ND (5)	2.2	Total cyanide qualified as minimum value
6505	65659	Influent to treatment	ND (5)	30.7	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6505	65731	Galley wastewater	ND (5)	12.9	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6505	65745	Biosolids	11	15.2	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6506	65896	Influent to treatment	ND (5)	45.5	
6506	65900	Influent to treatment	ND (5)	36.2	
6506	65904	Influent to treatment	ND (5)	75.6	
6506	65908	Influent to treatment	ND (5)	72.2	
6506	65912	Influent to treatment	ND (5)	76.5	

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: January 31, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Harry B. McCarty, Ph.D.
Senior Scientist

SUBJECT: Summary of Telephone Conversation with the Available Cyanide Laboratory

At your suggestion, I contacted the laboratory that ran the available cyanide analyses for Episodes 6503 to 6506 and asked about cross-contamination concerns, glassware washing procedures, and other aspects of the analysis that might explain the discrepancies between the total and available cyanide results. I spoke with John Sebroski, the laboratory director at Bayer Material Science on January 19, 2005. John gave me the following information:

- All of the "glassware" involved in the analysis is disposable. This includes the cups on the autosampler, the tubing on the flow injection system, etc. They do not reuse any of it, so there are no washing issues.

- The design of the flow injection instrumentation minimizes any concerns about carryover because the sample is injected into a continuous flow of solution that runs through the analyzer.

- They do run frequent blanks on the instrument, especially after QC samples such as the lab control sample (LCS or OPR). Those QC samples are run at relatively high levels, and there is no evidence of carryover or memory effects in the blanks. (I also confirmed this prior to calling him, using the data for these four episodes.)

- The OIA-1677 method has an ASTM counterpart that uses the same technique. There is a 2004 version of the ASTM standard that addresses the potential for sulfide interferences by introducing a bismuth nitrate reagent into the system to remove sulfides. John indicated that the use of the bismuth nitrate reagent could easily be accommodated using Method OIA-1677, since the instrumentation is the same as the ASTM standard.

- John indicated that sulfide problems for total cyanide are always a significant issue. He also said that the flow injection system for available cyanide can detect (and be affected by) sulfides at a much lower level than the field test methods will detect. Therefore, any sample not treated with lead carbonate in the field may well have an interference for available cyanide, even if the field test was negative for sulfides.

In summary, my conversation with Mr. Sebroski confirms much of the information SCC summarized in our lengthy discussion of the issues surrounding the total and available cyanide results for this project and generally rules out the chance that analytical concerns, such as carryover or glassware cleaning procedures, as an explanation for the observed cyanide results. Please do not hesitate to contact me at 703-461-2392, or by email at hmccarty@csc.com, if you have any questions.

Federal Sector
Civil Systems Development Division
6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020